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(54) Plastic lenses for spectacles

(57) [Problem] To provide plastic lenses for spectacles, having a high refractive index and a high Abbe's number, and having good transparency, heat resistance, mechanical strength and impact resistance.

[Means for Resolution] Provided are plastic lenses for spectacles, which are produced through polymerization of an epithio group-having compound (a), a polythiol compound (b) and a polyisocyanate compound (c) whereby the ratio of the polythiol compound (b) to the polyisocyanate compound (c) is at least 2.0 in case of a sulfur-free polyisocyanate compound (c_o) and is at least 1.2 in case of a sulfur-containing polyisocyanate compound (c_s), calculated on the basis of mol-amounts of -SH and -NCO groups

The invention also provides a process for preparing such lenses and a catalyst for use in said process.

Description

[Detailed Description of the Invention]

5 [Technical Field to which the Invention Belongs]

[0001] The present invention relates to plastic lenses for spectacles, in particular to those having a high refractive index and a high Abbe's number and having good transparency, heat resistance, mechanical strength and impact resistance.

[Prior Art]

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[0002] Plastics are being much used these days for optical products such as lenses, as being lightweight, hardly broken and easily colored when compared with glass. It is known to use, as the monomer material, an epithio group-having compound in producing plastic lenses. For example, Japanese Patent Laid-Open No. 180977/1999 discloses a plastic lens having optical properties, a refractive index of 1.70 or so and an Abbe's number of from 35 to 37 or so, which, however, still leaves room for improving its heat resistance and mechanical strength.

[0003] Japanese Patent Laid-Open Nos. 292950/1999 and 352302/1999 disclose a resin composition prepared by reacting an epithio group-having compound, an isocyanate group-having compound and a thiol group-having compound in a ratio of thiol group/isocyanate group of at most 1, and its use for plastic lenses. They say that the resin composition has improved heat resistance, mechanical strength and impact resistance. However, the plastic lenses of the resin composition are often cloudy and could not be well cured, and are therefore unsuitable to practical use for spectacles.

[Problems that the Invention is to Solve]

[0004] The present invention has been made so as to solve the problems as above, and its object is to provide plastic lenses for spectacles having a high refractive index and a high Abbe's number and having good transparency, heat resistance, mechanical strength and impact resistance.

[Means for Solving the Problems]

[0005] The present inventors have found that (1) a plastic lens produced through polymerization of an epithio grouphaving compound (a), a mercapto (-SH) group-having polythiol compound (b) and an isocyanate (-NCO) group-having, sulfur-free polyisocyanate compound (c₀) in a ratio (by mol), -SH/-NCO, of at least 2.0; (2) a plastic lens produced through polymerization of an epithio group-having compound (a), a mercapto group-having polythiol compound (b) and an isocyanate group-having, sulfur-containing polyisocyanate compound (c_s) in a ratio (by mol), -SH/-NCO, of at least 1.2 can attain the object.

[0006] Specifically, the first aspect of the invention is to provide a plastic lens for spectacles, which is produced through polymerization of an epithio group-having compound, a polythiol compound and a sulfur-free polyisocyanate compound in a ratio (by mol) of the polythiol compound to the sulfur-free polyisocyanate compound, -SH/-NCO, of being at least 2.0.

[0007] The second aspect of the invention is to provide a plastic lens for spectacles, which is produced through polymerization of an epithio group-having compound, a polythiol compound and a sulfur-containing polyisocyanate compound in a ratio (by mol) of the polythiol compound to the sulfur-containing polyisocyanate compound, -SH/-NCO, of being at least 1.2.

[0008] The polyisocyanate compound (c) may be a mixture of a sulfur-containing polyisocyanate compound (c_s) and a sulfur-free polyisocyanate compound (c_o).

[0009] Preferably the plastic lens material is produced through polymerization of at least one polyisocyanate compound selected from di(isocyanatomethyl)bicycloheptane, bis(isocyanatomethyl)-1,4-dithian and dicyclohexylmethane disocyanate, and an epithio group-having compound and a polythiol compound.

[0010] Also preferably the plastic lens material is produced through polymerization of a polyisocyanate compound prepared by mixing bis(isocyanatomethyl)-1.4-dithian with di(isocyanatomethyl)bicycloheptane and/or dicyclohexylmethane diisocyanate, and an epithio group-having compound and a polythiol compound.

[Modes of Carrying out the Invention]

[0011] In its first aspect, the plastic lens for spectacles of the invention is produced through polymerization of an

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epithio group-having compound, a polythiol compound and a sulfur-free polyisocyanate compound in a ratio (by mol) of the polythiol compound to the sulfur-free polyisocyanate compound, -SH/-NCO, of being at least 2.0. If the ratio -SH/-NCO is smaller than 2.0, the effect of the first aspect of the invention cannot be obtained.

[0012] In its second aspect, the plastic lens for spectacles of the invention is produced through polymerization of an epithio group-having compound, a polythiol compound and a sulfur-containing polyisocyanate compound in a ratio (by mol) of the polythiol compound to the sulfur-containing polyisocyanate compound, -SH/-NCO, of being at least 1.2. If the ratio -SH/-NCO is smaller than 1.2, the effect of the invention cannot be obtained. Polyisothiocyanate group-having compounds are outside the scope of the sulfur-containing polyisocyanate compound, as not producing the advantages of the invention.

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[0013] With the increase in the proportion of thiourethane bonds therein, lenses for spectacles could have an increased tensile strength characteristic of polythiourethanes, but their refractive index could not increase. For further increasing the refractive index of the lenses while the lenses are kept having an increased tensile strength and an increased Abbe's number, heretofore proposed is adding an epithio group-having compound to the lenses. However, in the system for lenses that comprises an epithio group-having compound, a polythiol compound and a sulfur-free polyisocyanate compound, if the polyisocyanate is excessive over the polythiol, as in the Examples in Japanese Patent Laid-Open Nos. 180977/1999 and 292950/1999, the lenses formed are cloudy.

[0014] On the other hand, lenses formed from a sulfur-containing polyisocyanate compound, an epithio group-having compound and a polythiol compounds are not cloudy even when the proportion of the sulfur-containing polyisocyanate compound therein is increased. Since the sulfur content and the thiourethane bond content thereof are high, the lenses have an increased refractive index and their mechanical strength and Abbe's number are not lowered.

[0015] Some sulfur-containing polyisocyanate compounds such as bis(isocyanatomethyl)-1,4-dithian are solid at room temperature. Such a solid, sulfur-containing polyisocyanate compound may be dissolved in a sulfur-free polyisocyanate compound that is liquid at room temperature. As being liquid at room temperature, the resulting mixture is casy to handle when it is used in producing lenses. In mixing the two, the ratio of the sulfur-containing polyisocyanate compound to the sulfur-free polyisocyanate compound may be so controlled that the liquid, sulfur-free polyisocyanate compound can dissolve the solid, sulfur-containing polyisocyanate compound to give a mixture that is liquid at room temperature. Concretely, the ratio of the two, the sulfur-containing polyisocyanate compound and the sulfur-free polyisocyanate compound may be such that the amount of the sulfur-free polyisocyanate compound is enough for dissolving therein the sulfur-containing polyisocyanate compound which is solid at room temperature. The ratio of the two is not specifically defined. For example, from 5 to 30 parts by weight of a sulfur-free polyisocyanate may be added to 10 parts by weight of a sulfur-containing polyisocyanate.

[0016] Preferably, the sulfur-free polyisocyanate compound to be used in the first and second aspects of the invention is di(isocyanatomethyl)bicycloheptane and/or dicyclohexylmethane diisocyanate.

[0017] The sulfur-containing polyisocyanate compound to be used is preferably bis(isocyanatomethyl)-1,4-dithian.

[0018] The lens for spectacles may be produced through polymerization of at least one polyisocyanate compound selected from di(isocyanatomethyl)bicycloheptane, bis(isocyanatomethyl)-1,4-dithian and dicyclohexylmethane disocyanate. and an epithio group-having compound and a polythiol compound.

[0019] The lens for spectacles may also be produced through polymerization of a polyisocyanate compound prepared by mixing bis(isocyanatomethyl)-1,4-dithian with di(isocyanatomethyl)bicycloheptane and/or dicyclohexylmethane disocyanate, and an epithio group-having compound and a polythiol compound.

[0020] Bis(isocyanatomethyl)-1,4-dithian is solid at room temperature. When it is mixed with di(isocyanatomethyl) bicycloheptane and/or dicyclohexylmethane diisocyanate, and dissolved therein, the resulting mixture is liquid at room temperature, and is easy to handle.

[0021] The ratio (by mol) of the polythiol compound to the polyisocyanate compound, -SH/-NCO, is preferably at least 2.0, more preferably at least 2.5.

[0022] The polythiol compound for use in the invention includes, for example, aliphatic thiols such as methanedithiol, 1,2-ethanedithiol, 1,1-propanedithiol, 1,2-propanedithiol, 1,3-propanedithiol, 2,2-propanedithiol, 1,6-hexanedithiol, 1,2,3-propanetrithiol, tetrakis(mercaptomethyl)methane, 1,1-cyclohexanedithiol, 1,2-cyclohexanedithiol, 2,2-dimethyl-propane-1,3-dithiol, 3,4-dimethoxybutane-1,2-dithiol, 2-methylcyclohexane-2,3-dithiol, 1,1-bis(mercaptomethyl)cyclohexane, bis(2-mercaptoethyl) thiomalate, (2-mercaptoethyl) 2,3-dimercaptosuccinate, 2,3-dimercapto-1-propanol (2-mercaptoacetate), 2,3-dimercapto-1-propanol (3-mercaptoacetate), diethylene glycol bis(2-mercaptoacetate), diethylene glycol bis(3-mercaptopropionate), 1,2-dimercaptopropyl methyl ether, 2,3-dimercaptopropyl methyl ether, 2,2-bis(mercaptomethyl)-1,3-propanedithiol, bis(2-mercaptoethyl) ether, ethylene glycol bis(2-mercaptoacetate), ethylene glycol bis(3-mercaptopropionate), trimethylolpropane tris(2-mercaptoacetate), trimethylolpropane tris(3-mercaptopropionate), pentaerythritol tetrakis(2-mercaptoacetate), pentaerythritol tetrakis(3-mercaptopropionate), 1,2-bis (2-mercaptoethylthio)-3-mercaptopropane; aliphatic thiols having sulfur atom(s) in addition to mercapto groups, such as bis(mercaptomethylthio)methane, bis(3-mercaptopropyl)methane, 1,2-bis(mercaptomethylthio)ethane, 1,2-bis(merca

(2-mercaptoethylthio)ethane, 1,2-(3-mercaptopropyl)ethane, 1,3-bis(mercaptomethylthio)propane, 1,3-bis(2-mercaptopropyl)ethane, 1,3-bis(mercaptomethylthio)propane, 1,3-bis(2-mercaptopropyl)ethane, 1,3-bis(mercaptomethylthio)propane, 1,3-bis(2-mercaptopropyl)ethane, 1,3-bis(mercaptomethylthio)propane, 1,3-bis(2-mercaptopropyl)ethane, 1,3-bis(3-mercaptopropyl)ethane, 1,3-bis(3-mercaptopropyl)eth toethylthio)propane, 1,3-bis(3-mercaptopropylthio)propane, 1,2-bis(2-mercaptoethylthio)-3-mercaptopropane, 2-mercaptopropane, 2 captoethylthio-1,3-propanedithiol, 1,2,3-tris(mercaptomethylthio)propane, 1,2,3-tris(2-mercaptoethylthio)propane, 1,2,3-tris(3-mercaptopropylthio)propane, tetrakis(mercaptomethylthiomethyl)methane, tetrakis(2-mercaptoethylthiomethyl) omethyl)methane, tetrakis(3-mercaptopropylthiomethyl)methane, bis(2,3-dimercaptopropyl) sulfide, 2,5-dimercapto-1,4-dithian, bis(mercaptomethyl) disulfide, bis(mercaptoethyl) disulfide, bis(mercaptopropyl) disulfide, and their thioglycolates and mercaptopropionates, hydroxymethylsulfide bis(2-mercaptoacetate), hydroxymethylsulfide bis(3-mercaptoacetate) topropionate), hydroxyethylsulfide bis(2-mercaptoacetate), hydroxyethylsulfide bis(3-mercaptopropionate), hydroxyethyls propylsulfide bis(2-mercaptoacetate), hydroxypropylsulfide bis(3-mercaptopropionate), hydroxymethyldisulfide bis (2-mercaptoacetate), hydroxymethyldisulfide bis(3-mercaptopropionate), hydroxyethyldisulfide bis(2-mercaptoacetate), hydroxyethyldisulfide bis(3-mercaptopropionate), hydroxypropyldisulfide bis(2-mercaptoacetate), hydroxypropyldisulfide bis(3-mercaptopropionate), 2-mercaptoethyl-ether bis(2-mercaptoacetate), 2-mercaptoethyl-ether bis (3-mercaptopropionate), 1,4-dithian-2,5-diol bis(2-mercaptoacetate), 1,4-dithian-2,5-diol bis(3-mercaptopropionate), bis(2-mercaptoethyl) thioglycolate, bis(2-mercaptoethyl) thiodipropionate, bis(2-mercaptoethyl) 4,4'-thiodibutyrate, bis (2-mercaptoethyl) dithiodiglycolate, bis(2-mercaptoethyl) dithiodipropionate, bis(2-mercaptoethyl) 4,4'-dithiodibutyrate, bis(2,3-dimercaptopropyl) thiodiglycolate, bis(2,3-dimercaptopropyl) thiodipropionate, bis(2,3-dimercaptopropyl) dithiodiglycolate, (2,3-dimercaptopropyl) dithiodipropionate, 4-mercaptomethyl-3,6-dithiaoctane-1,8-dithiol, bis (mercaptomethyl)-3,6,9-trithia-1,11-undecanedithiol, bis(1,3-dimercapto-2-propyl) sulfide; and heterocyclic compounds having sulfur atom(s) in addition to mercapto groups, such as 3,4-thiophenedithiol, tetrahydrothiophene-2,5-dimercaptomethyl, 2,5-dimercapto-1,3,4-thiadiazole, 2,5-dimercapto-1,4-dithian, 2,5-dimercaptomethyl-1,4-dithian

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[0023] The polythiol compound for use in the invention is preferably bismercaptomethyl-1,4-dithian and/or (4-mercaptomethyl-2,5-dithianyl)methyl disulfide.

[0024] The epithio group-having compound for use in the invention is an episulfide monomer, including, for example, alicyclic skeleton-having episulfide compounds such as 1,3- and 1,4-bis(β-epithiopropylthio)cyclohexanes, 1,3- and 1,4-bis(β-epithiopropylthio)cyclohexyl]methane, 2,2-bis[4-(β-epithiopropylthio)cyclohexyl]methane, 2,2-bis[4-(β-epithiopropylthio)cyclohexyl]methane, 2,2-bis[4-(β-epithiopropylthio)cyclohexyl] sulfide; aromatic skeleton-having episulfide compounds such as 1,3- and 1,4-bis(β-epithiopropylthio)benzenes, 1,3- and 1,4-bis(β-epithiopropylthiomethyl)benzenes, bis[4-(β-epithiopropylthio)phenyl]methane, 2,2-bis[4-(β-epithiopropylthio)phenyl]propane, bis[4-(β-epithiopropylthio)phenyl] sulfide, bis[4-(β-epithiopropylthio)phenyl] sulfine, 4,4-bis(β-epithiopropylthio)biphenyl; dithian skeleton-having episulfide compounds such as 2,5-bis(β-epithiopropylthiomethyl)-1,4-dithian, 2,5-bis(β-epithiopropylthioethyl)-1,4-dithian, 2,3-tri(β-epithiopropylthioethyl)-1,4-dithian; and aliphatic skeleton-having episulfide compounds such as 2-(2-β-epithiopropylthioethylthio)-1,3-bis(β-epithiopropylthiomethyl) propane, 1,2-bis[(2-β-epithiopropylthioethyl))thio]-3-(β-epithiopropylthio) propane, tetrakis(β-epithiopropylthiomethyl) methane, 1,1,1-tris(β-epithiopropylthiomethyl) propane, bis(β-epithiopropyl) sulfide.

[0025] Many epithio group-having compounds are known, and their examples are described in, for example, Japanese Patent Laid-Open Nos. 071580/1997, 110979/1997, 255781/1997, 081320/1991, 140070/1999, 183702/1999, 189592/1999, 180977/1999, and Japanese Patent Re-Laid-Open No. 810575/1989. Episulfide monomers disclosed in these publications are all usable in the invention.

[0026] Of the epithio group-having compounds mentioned hereinabove, bis(β -epithiopropyl) sulfide is preferred for use in the invention.

[0027] Preferably, the plastic lenses for spectacles of the invention that comprise the above-mentioned bis(β-epith-iopropyl) sulfide preferably contain from 60 to 85% by weight of the epithio group-having compound and from 15 to 40% by weight of the polythiol compound and the polyisocyanate compound in total, in order that they have a refractive index of 1.70 or so and an Abbe's number of 36 or so and their mechanical strength is enough for practical use of the lenses in rimless spectacles.

[0028] Especially preferred combinations of the polyisocyanate compound, the polythiol compound and the epithio group-having compound for use in the invention are mentioned below.

- <1> Di(isocyanatomethyl)bicycloheptane (polyisocyanate compound), bis(mercaptomethyl)-1,4-dithian (polythiol compound), and bis(β -epithiopropyl) sulfide (epithio group-having compound).
- <2> Di(isocyanatomethyl)bicycloheptane (polyisocyanate compound), (4-mercaptomethyl-2,5-dithianyl)methyl disulfide, bis(mercaptomethyl)-1,4-dithian (polythiol compounds), and bis(β-epithiopropyl) sulfide (epithio grouphaving compound).
- <3>-Bis(isocyanatomethyl)-1,4-dithian_(polyisocyanate_compound), bis(mercaptomethyl)-1,4-dithian (polythiol compound), and bis(β-epithiopropyl) sulfide (epithio group-having compound).
- <4> Dicyclohexylmethane diisocyanate (polyisocyanate compound), (4-mercaptomethyl-2,5-dithianyl)methyl disulfide, bis(mercaptomethyl)-1,4-dithian (polythiol compounds), and bis(β -epithiopropyl) sulfide (epithio group-

having compound).

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<5> Bis(isocyanatomethyl)-1,4-dithian and di(isocyanatomethyl)bicycloheptane (polyisocyanate compounds), bis (mercaptomethyl)-1,4-dithian (polythiol compound), and bis(β-epithiopropyl) sulfide (epithio group-having compound).

<6> Bis(isocyanatomethyl)-1,4-dithian and dicyclohexylmethane diisocyanate (polyisocyanate compounds), bis (mercaptomethyl)-1,4-dithian (polythiol compound), and bis(β-epithiopropyl) sulfide (epithio group-having compound)

[0029] Preferably, a catalyst of the following general formula (1) is added to the plastic lenses for spectacles of the invention while they are produced through polymerization. The catalyst facilitates the production of lenses with neither optical strain nor striae from the polymerizing compounds, epithio group-having compound, polythiol compound and polyisocyanate compound.

CH, COO-
$$\frac{R}{I}$$
 | R | CH, COO- $\frac{R}{I}$ | CH, COOCH; ... (1)

wherein R indicates an alkyl group having from 1 to 4 carbon atoms.

[0030] Preferably, the catalyst of formula (1) is at least one selected from tetramethyldiacetoxy-distannoxane, tetra-ethyldiacetoxy-distannoxane, tetrapropyldiacetoxy-distannoxane and tetrabutyldiacetoxy-distannoxane.

[0031] In case where the plastic lenses of the invention are, after produced through polymerization in a mold, difficult to release from the mold, any known external and/or internal lubricant may be used for them or may be added to them to thereby improve the releasability of the lenses. If desired, an UV absorbent may be added to the lenses while they are produced. This is for protecting the resin of the lenses from UV rays and also for protecting the eye from them, and its amount to be added to each lens may fall generally between 0.03% and 3% or so, though depending on its UV absorbability and on the maximum wavelength of the UV rays to be absorbed by it. As the case may be, the lenses produced may be dipped in an UV absorbent. The plastic lenses of the invention are easy to color with a colorant.

[0032] For improving their scratch resistance, the plastic lenses of the invention may be coated with a hard film, for which is usable a coating liquid that contains an organosilicon compound or acrylic compound and inorganic fine particles of, for example, tin oxide, silicon oxide, zirconium oxide or titanium oxide. For improving their impact resistance, the plastic lenses may be coated with a primer layer that consists essentially of polyurethane.

[0033] For preventing them from glaring, the hard film of the plastic lenses may be further coated with an anti-glare film that contains an inorganic substance of, for example, silicon oxide, titanium dioxide, zirconium oxide or tantalum oxide. For improving their water repellency, the anti-glare film of the plastic lenses may be coated with a water-repellent film of an organic fluorosilicon compound.

[0034] The plastic lenses for spectacles of the invention mentioned hereinabove have a refractive index of from 1.65 to 1.76, and their mechanical strength is higher than that of conventional plastic lenses. In addition, they are highly transparent, and have good heat resistance and impact resistance.

45 [Examples]

[0035] The invention is described in more detail with reference to the following Examples, which, however, are not intended to restrict the scope of the invention.

[0036] The physical properties of the plastic lenses for spectacles produced in the following Examples and Comparative Examples are measured according to the methods mentioned below.

(1) Refractive index and Abbe's number:

[0037] Measured at 20°C with a precision refractometer, Kalnew's KPR-200 Model.

(2) Heat resistance:

[0038] Measured with a thermal analyzer, Rigaku-sha's TAS-100, TMA8140, according to a penetration method (in

which the thickness of the sample analyzed is 3 mm, the pin diameter is 0.5 mm, the load is 10 g, and the heating rate is 10°C/min). The peak temperature at which the thermal expansion of the sample has changed is read, and this indicates the heat resistance of the sample.

5 (3) Tensile strength:

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[0039] A lens prepared to have a power of 0.00 D, a diameter of 80 mm and a thickness of 1.8 mm is worked to be fittable to a frame of an electronic universal tester (Yonekura Seisakusho's Model CATY200WR). In this, two holes each having a diameter of 1.6 mm are drilled at opposite ends. The thus-worked lens sample is fixed to the tester with 1.6 mm¢ pins fitted to its holes, and pulled at a stress rate of 0.05 mm/min, and the tensile strength at break of the sample is measured.

- (4) Presence or absence of striae:
- 15 [0040] Each sample is macroscopically checked as to whether or not it has striae, according to the schlieren method. The samples thus checked are evaluated on the basis of the following criteria:
 - O: No striae found.
 - · : Striae found.

Example 1:

[0041] 80.0 parts by weight of an epithio group-having compound, bis(β-epithiopropyl) sulfide, 15.65 parts by weight of a polythiol compound, bis(mercaptomethyl)-1,4-dithian, and 4.35 parts by weight of a polyisocyanate compound, di (isocyanatomethyl)bicycloheptane were mixed with stirring along with 50 ppm of an internal lubricant, a mixture of dibutoxyethyl acid phosphate and butoxyethyl acid phosphate, to which were added 0.01 parts by weight of tetranbutyl-1.3-diacetoxy-distannoxane and 0.05 parts by weight of tetrabutylphosphonium bromide both serving as a catalyst. These were stirred and mixed under a reduced pressure of 10 mmHg for about 3 minutes to prepare a monomer composition for lenses. The ratio of -SH/-NCO in this composition is given in Table 1.

[0042] Next, the monomer composition was cast into a glass mold for lenses (lens power 0.00 D, lens diameter 80 mm. lens thickness 1.8 mm), which had been previously prepared and equipped with a resin gasket. The mold was put into an electric furnace, and gradually heated therein at from 20°C up to 100°C over a period of 20 hours and then kept heated at 100°C for 30 minutes, through which the monomers were polymerized.

[0043] After having been thus polymerized, the lens was released from the mold, and then further heated at 110°C for 1 hour. It was visually checked for outward appearance, and tested for (1) to (4) as above. The results are given in Table 1.

Examples 2 to 10:

[0044] Lenses were produced in the same manner as in Example 1, except that the epithio group-having compound, the polythiol compound and the polyisocyanate compound and their amounts were varied as in Table 1. The lenses were visually checked for appearance, and tested for (1) to (4) as above. The results are given in Table 1.

Comparative Example 1:

[0045] 75.0 parts by weight of an epithio group-having compound, bis(β-epithiopropyl) sulfide, 5.0 parts by weight of a polythiol compound, n-butyl thioglycolate, and 20.0 parts by weight of a polyisocyanate compound, m-xylene diisocyanate were mixed with stirring, to which was added 0.05 parts by weight of a catalyst, tetrabutylphosphonium bromide. These were stirred and mixed under a reduced pressure of 10 mmHg for about 3 minutes to prepare a monomer composition for lenses. The ratio of -SH/-NCO in this composition is given in Table 1.

[0046] Next, the monomer mixture was polymerized in the same manner as in Example 1. However, the product obtained was dark brown liquid and was not resinous. Therefore, this was not tested for (1) to (4).

Comparative Example 2:

[0047] The monomers were polymerized in the same manner as in Comparative Example 1, except that dimercaptoethyl sulfide was used in place of n-butyl thioglycolate.

[0048] However, the product obtained was milky, opaque jelly. Therefore, this was not tested for (1) to (4).

Comparative Example 3:

[0049] 80.0 parts by weight of an epithio group-having compound, bis(β-epithiopropyl) sulfide, 5.0 parts by weight of a polythiol compound, n-butyl thioglycolate, and 15.0 parts by weight of a polyisocyanate compound, isophorone disocyanate were mixed with stirring, to which was added 0.05 parts by weight of a catalyst, tetrabutylphosphonium bromide. These were stirred and mixed under a reduced pressure of 10 mmHg for about 3 minutes to prepare a monomer composition for lenses. The ratio of -SH/-NCO in this composition is given in Table 1.

[0050] Next, the monomer mixture was polymerized in the same manner as in Example 1. However, the product obtained was dark brown liquid and was not resinous. Therefore, this was not tested for (1) to (4).

Comparative Example 4:

[0051] 80.0 parts by weight of an epithio group-having compound, bis(β-epithiopropyl) sulfide, 20.0 parts by weight of a polythiol compound, 1,2-bis((mercaptoethyl)thio)-3-mercaptopropane, and 20.0 parts by weight of a polyisocyanate compound, m-xylene diisocyanate were mixed with stirring, to which was added 0.05 parts by weight of a catalyst, dibutyltin dichloride. These were stirred and mixed under a reduced pressure of 10 mmHg for about 3 minutes to prepare a monomer composition for lenses. The ratio of -SH/-NCO in this composition is given in Table 1.

[0052] Next, the monomer composition was cast into a glass mold for lenses (lens power 0.00 D, lens diameter 80 mm, lens thickness 1.8 mm), which had been previously prepared and equipped with a resin gasket. The mold was put into an electric furnace, and gradually heated therein at from 20°C up to 120°C over a period of 20 hours and then kept heated at 120°C for 30 minutes, through which the monomers were polymerized.

[0053] However, the resin thus obtained was like soft rubber, and had an offensive smell and was much yellowed. Therefore, this was not tested for (1) to (4).

Comparative Example 5:

[0054] 93.0 parts by weight of an epithio group-having compound, bis(β-epithiopropyl) sulfide, 6.0 parts by weight of a polythiol compound, dimercaptoethyl sulfide, and 1.0 part by weight of hydroxyethyl methacrylate were mixed with stirring, to which was added 0.05 parts by weight of a catalyst, tetrabutylphosphonium bromide. These were stirred and mixed under a reduced pressure of 10 mmHg for about 3 minutes to prepare a monomer composition for lenses. The ratio of -SH/-NCO in this composition is given in Table 1.

[0055] Next, the monomer mixture was polymerized in the same manner as in Example 1. The lens obtained was visually checked for appearance, and tested for (1) to (4) as above. The results are given in Table 1.

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5	Striae	ij.	٥	5 .	9	0	0	÷	o	O	0					•
10	Tensile Strength kgf	40	40	23	44	53	ያ	99	49	54	51					25
15	Heat Resistance UUU	06	92	06	82	68	92	96	68	92	95	Not cured (dark brown liquid)	Not cured (milky, opaque jelly)	Not cured (dark brown liquid)	Yellowed soft rubber	06
. 20	Abbe's Number	36	36	38	36	36	96	98	36	36	æ	N (dark	(milky.) (dark	Yellow	æ
	Refractive Index	1.699	1.699	1.700	1.691	1:697	1.696	1.695	1.694	1.694	1.694					1.700
25	Appearance	colorless	colorless transparent	colorless transparent	coloriess	colorless	colorless	colorless	colorless	colorless	coloriess transparent					colorless transparent
30	Epithio group-having Compound	BEPS 80.0	BEPS 75.0	BEPS 65.0	BEPS 70.0	BEPS 67.50	BEPS 67.50	BEPS	BEPS	BEPS 70.00	BEPS 70.00	BEPS 75.0	BEPS 75.0	BEPS 80.0	BEPS 60.0	BEPS 93.0
35	Blend Ratio (-SH/-NCO) by mol	3.5	3.0	3.0	3.0	1.80	1.50	1.25	1.80	1.75	1.50	0.16	0.31	0.25	1.08	
40	Polythiol Compound wt.pls.	BMMD	MMDS/BMMD	BMMD 25.70	MMDS/BMMD	BMMD	BMMD 19 961	BMMD	BMMD	19.02 BMMD 18.82	BMMD 17.64	BTG 5.00	DMES 5.00	BTG 5.00	DMTMP	DMES/HEMA 6.00/1.00
45	Polyisocyanate Compound wt.pts.	DIMB	OIMB 5.46	BIMD	HMDI	BIMD	BIMD	13.64 BIMD	15.10 BIMD/DIMB	6.88/4.10 BIMD/DIMB	BIMD/DIMB 8 93/3.43	XDI 20.00	10x	IPDI 1500	IQX 6	
50		-	2	3	4	2	9		80	6	9	-	2	m	4	2
		Example	_l .—	.1.						-		Comparative				

Notes:

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DIMB: di(isocyanatomethyl)bicycloheptane

BIMD: bis(isocyanatomethyl)-1,4-dithian

HMDI: dicyclohexylmethane diisocyanate

BMMD: bis(mercaptomethyl)-1,4-dithian

MMDS: (4-mercaptomethyl-2,5-dithianyl)methyl disulfide

BEPS: bis(β-epithiopropyl) sulfide

XDI: m-xylene diisocyanate

IPDI: isophorone diisocyanate

BTG: n-butyl thioglycolate

DMES: dimercaptoethyl sulfide

DMTMP: 1,2-bis((mercaptoethyl)thio)-3-mercaptopropane

HEMA: hydroxyethyl methacrylate

[0056] As in Table 1, the lenses of Examples 1 to 10 are all colorless transparent, and have a high refractive index and a high Abbe's number, and their heat resistance and tensile strength are all good.

[Advantages of the Invention]

[0057] As described in detail hereinabove, the plastic lenses for spectacles of the invention have a high refractive index and a high Abbe's number. They are transparent, and have good heat resistance, mechanical strength and impact resistance. Therefore, they are suitable to spectacles.

Claims

- 1. Process for preparing a material suitable for a plastic lens for spectacles which process comprises polymerizing an epithio group-having compound (a), a polythiol compound (b) and a polyisocyanate compound (c) characterized in that the ratio of the polythiol compound (b) to the polyisocyanate compound (c) is at least 2.0 in case of a sulfur-free polyisocyanate compound (c_o) and is at least 1.2 in case of a sulfur-containing polyisocyanate compound (c_o), calculated on the basis of mol-amounts of -SH and -NCO groups.
- 2. Process according to claim 1 employing from 60 to 85% by weight of the epithio group-having compound (a) and from 15 to 40% by weight of the polythiol compound (b) and the polyisocyanate compound (c) in total.
 - 3. Process according to claim 1 or 2 wherein the sulfur-free polyisocyanate compound (c_o) is di(isocyanatomethyl) bicycloheptane and/or dicyclohexylmethane diisocyanate.
- 55 4. Process according to any of claims 1-3, wherein the sulfur-containing polyisocyanate compound (c_s) is bis(isocyanatomethyl)-1,4-dithian.
 - 5. Process according to any of claims 1-4 wherein the polyisocyanate compound (c) is selected from di(isocyanato-

methyl)bicycloheptane, bis(isocyanatomethyl)-1,4-dithian and dicyclohexylmethane diisocyanate.

- 6. Process according to any of claims 1-5 wherein the polyisocyanate compound (c) is a mixture of bis(isocyanatomethyl)-1,4-dithian with di(isocyanatomethyl)bicycloheptane and/or dicyclohexylmethane diisocyanate.
- 7. Process according to any of claims 1-6 wherein the polythiol compound (b) is bismercaptomethyl-1,4-dithian and/ or (4-mercaptomethyl-2,5-dithianyl)methyl disulfide.
- Process according to any of claims 1-7 wherein the epithio group-having compound (a) is bis(β-epithiopropyl)
 sulfide.
 - 9. Process according to any of claims 1-8 wherein a catalyst of the following general formula (1):

wherein R indicates an alkyl group having from 1 to 4 carbon atoms, is added.

- 10. Process according to claim 9 wherein the catalyst of formula (1) is at least one selected from tetramethyldiacetoxy-distannoxane, tetrapropyldiacetoxy-distannoxane and tetrabutyldiacetoxy-distannoxane.
 - 11. Catalyst for use in the process according to any of claims 1-8 having the general formula

CH; COO-
$$\frac{R}{S}$$
 $\frac{R}{I}$ $\frac{I}{I}$ -OCOCH; ... (1)

wherein R indicates an alkyl group having from 1 to 4 carbon atoms

- 12. Catalyst according to claim 11 which is tetramethyldiacetoxy-distannoxane, tetraethyldiacetoxy-distannoxane, tetrapropyldiacetoxy-distannoxane or tetrabutyldiacetoxy-distannoxane.
 - 13. Plastic lens for spectacles made of a material obtainable according to the process of any of claims 1-10.
- 45 14. Plastic lens according to claim 13 which is coated with a hard film of an organosilicon compound.
 - 15. Plastic lens according to claim 14 whereby hard film is further coated with an anti-glare film of an inorganic substance.
- 16. Plastic lens according to claim 15 whereby the anti-glare film is further coated with a water-repellent film of a fluorine-containing silicon compound.
 - 17. Plastic lens according to any of claims 13-16 which has a refractive index of from 1.65 to 1.76.

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(54) Plastic lenses for spectacles

(57) [Problem] To provide plastic lenses for spectacles, having a high refractive index and a high Abbe's number, and having good transparency, heat resistance, mechanical strength and impact resistance.

[Means for Resolution] Provided are plastic lenses for spectacles, which are produced through polymerization of an epithio group-having compound (a), a polythiol compound (b) and a polyisocyanate compound (c) whereby the ratio of the polythiol compound (b) to the

polyisocyanate compound (c) is at least 2.0 in case of a sulfur-free polyisocyanate compound (c_o) and is at least 1.2 in case of a sulfur-containing polyisocyanate compound (c_s), calculated on the basis of mol-amounts of -SH and -NCO groups

The invention also provides a process for preparing such lenses and a catalyst for use in said process.

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EUROPEAN SEARCH REPORT

Application Number EP 01 10 5357

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